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Production pattern of alkenones in the Mediterranean Sea

Yann Ternois¹, Marie-Alexandrine Sicre², Anne Boireau¹, Jean-Claude Marty³, and Juan-Carlos Miquel⁴

Abstract. Time-series of downward alkenone fluxes have been investigated at 200 m depth over a one year sediment trap experiment, in the Northwestern Mediterranean Sea. Alkenone flux maxima occurred in autumn and to a lesser extent in May, during the spring bloom. Temperature estimates calculated from the U_{37}^K index revealed that alkenone producers preferentially develop in subsurface waters (at about 50 m) in spring, whereas the autumn alkenone production occurred upper in the water column (around 30 m). Examination of the core-top U_{37}^K index values at various sites of the Northwestern Mediterranean basin, suggested that the spring bloom period do not significantly imprint the temperatures recorded in the sediments. The sedimentary temperature estimates would rather reflect annually integrated SST, with a major influence of the autumnal post-bloom development of the coccolithophores in the euphotic zone.

Introduction

Paleoclimatic studies focus on climate variability on a global scale. Such changes are evaluated using diverse approaches generally based on the ability of organisms to adjust and record changing environmental conditions either in their hard or soft components. One example of the flexibility of the organisms to develop an adaptative biochemistry are the alkenones. The within class distribution of this series of lipid constituents, encompassing C_{37} - C_{39} di-, tri- and tetra-unsaturated methyl and ethyl ketones, has been shown to be sensitive to growth temperature. Volkman *et al.* [1980] first reported alkenones and the related alkyl alkenoates in the marine coccolithophorid *Emiliania huxleyi*. Since then, other sources have been identified [e.g. Conte *et al.*, 1994]. The degree of unsaturation of these compounds, the U_{37}^K index, is related to surface water temperature [Marlowe, 1984; Brassell *et al.*, 1986]. The term U_{37}^K is defined as:

$$U_{37}^K = (C_{37:2}) / \{ (C_{37:2}) + (C_{37:3}) \}$$

where $(C_{37:2})$ and $(C_{37:3})$ are the concentrations of the di- and

tri-unsaturated C_{37} methyl alkenones, respectively. Results from culture experiments and oceanic waters have demonstrated a quasi-linear relationship between the temperature of alkenone production and the U_{37}^K index in warm waters [Marlowe, 1984; Prahl and Wakeham, 1987; Prahl *et al.*, 1988; Conte and Eglinton, 1993; Sikes and Volkman, 1993]. Recently, Ternois *et al.* [in press] calibrated the U_{37}^K index versus *in situ* temperatures for the Mediterranean Sea. In this region, the paleo-temperature reconstruction based on foraminiferal assemblages is difficult, due to the fact that good modern analogs are hard to obtain for glacial fossil samples. Because of this limitation, alkenones provide an alternative to the reconstruction of paleo-temperatures.

Refinement of the alkenone-based sea surface temperature estimation methods requires a better understanding of the biomarker production cycle. The most comprehensive means to better constrain the use of alkenone unsaturation index is to acquire relevant data seeking to characterize the depth and timing of alkenone production in the modern ocean. This work presents alkenone data obtained from a one year sediment trap deployment at 200 m in the open Northwestern Mediterranean Sea conducted as part of the DYFAMED (France-JGOFs) time-series program, and from surface sediments. The study's objective was to evaluate the applicability of U_{37}^K for the reconstruction of paleo-temperatures in the Mediterranean Sea.

Sampling and Methods

Sediment traps were deployed at 200 m depth in the Ligurian Sea, from February 1989 to March 1990 (station 1, Figure 1) with some interruptions. This site is located 45 km offshore Nice in the Northwestern Mediterranean basin, in the Ligurian Sea. The water depth at the site is about 2300 m. The sediment traps used (Technicap model PPS3) were cylindrical with a height of 1.9 m, a height/width ratio of 2.5 in the cross cylindrical portion and a collection section of 0.125 m². They were equipped with a pre-programmed 6 cup collector to collect six discrete samples with a 9 to 15 day sampling duration. Swimmers were removed from the samples before freeze-drying.

Piston and box cores were collected from various sites in the Northwestern Mediterranean Sea (Figure 1) during two cruises aboard the Marion Dufresne R/V in 1990 and 1991 (Table 1). Sub-samples (0-1 cm for BC samples and 5-6 cm for MD samples) were taken from each core using a stainless steel spatula, then wrapped in an aluminium foil and stored until analysis in the laboratory. Samples labelled as BC were frozen at -18°C whereas those labelled as MD were stored at 4°C. The surface sediment (0-1 cm) at station 1 was also collected. Methods for POC determinations are described in Miquel *et al.* [1994]. Organic carbon was measured in the sediment trap material by high temperature oxidation using a Heraeus CHN-O- Rapid analyzer. Carbonates were removed before analysis with 1M H_3PO_4 and at least two replicates of each

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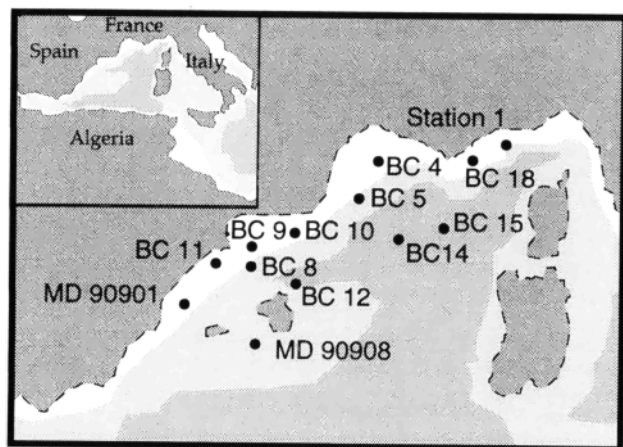


Figure 1. Map showing the sediment trap location (station 1) and sediment core locations in the Northwestern Mediterranean sea.

sample were run to reduce bias due to the potential sample heterogeneity.

Approximately 25 mg of each freeze-dried sediment trap sample was extracted twice with 5 ml of methylene chloride and a third time with 5 ml of methanol. For each extraction the samples were ultrasonicated and centrifuged at 2000 rotations/min for 10 minutes. The total extracts were concentrated to just dryness using a rotary evaporator, and transferred to 4 ml vials. Freeze-dried sediments were extracted following the same procedure as described above for sediment trap samples.

Lipid extracts from the sediment and sediment trap material were then partitioned into compound classes following the procedure described by *Peltzer et al.* [1984]. The fractions containing the alkenones were concentrated, transferred to vials and evaporated under a nitrogen stream. They were then analyzed on a Delsi DI 200 gas chromatograph equipped with a fused silica capillary column (50 m x 0.32 mm i.d. CP-Sil5, Chrompack) and a flame ionization detector. Helium was used as a carrier gas. The oven temperature was programmed from 50°C to 100°C at 25°C. min⁻¹ and from 100°C to 295°C at 5°C. min⁻¹. Quantitation of alkenones was achieved using α -cholestane, added to the sample prior to injection. Compounds were quantified using the Apex PC based chromatograph software. The accuracy of alkenone concentration determination was about 10%.

Results and Discussion

Sediment Trap Data

Figures 2a-b show the temporal variability of organic carbon and alkenone fluxes at 200 m depth from February 1989 to March 1990, in the Ligurian Sea. Estimated temperatures, calculated from the calibration established for the Mediterranean waters by *Ternois et al.* [in press] ($U_{37}^K = 0.041T - 0.21$, $r^2 = 0.97$, $n = 20$), are also reported in figure 2b. From this record, alkenone production appears strongly seasonal. The maximum alkenone flux occurred in October. A smaller production maximum occurred during the last two weeks of May which coincided with the spring bloom period. Estimated U_{37}^K temperatures were approximately 17°C in

Table 1. Sediment Sampling Location, U_{37}^K , and Temperature Estimates Calculated from the Calibration for Mediterranean Waters ($U_{37}^K = 0.041T - 0.21$, $r^2 = 0.97$, $n = 20$; *Ternois et al.*, in press). Monthly Temperatures from *Levittus* [1982] Are also Indicated for Each Sediment.

Sample name	Location	U_{37}^K	T°C	Levittus temperatures											
				Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	
MD 90901	39°56'N; 1°35'E	0.62	20.1	14.5	13.7	13.5	14.8	17.1	20.7	23.9	25.2	24.3	20.9	18.5	
MD 90908	36°06'N; 2°56'E	0.60	19.4	14.4	14.4	13.9	15.6	16.8	20.8	24.1	24.8	23.8	18.7	19.0	
BC4	43°09'N; 4°40'E	0.54	18.1												
BC11	40°30'N; 0°43'E	0.57	18.8												
BC14	42°00'N; 4°40'E	0.59	19.2	13.3	12.7	12.6	13.8	15.2	19.4	21.3	22.0	20.5	19.6	16.6	
BC18	42°45'N; 6°10'E	0.62	19.9	13.6	13.2	13.1	14.1	16.0	19.9	22.3	22.6	21.5	20.2	17.1	
BC9	40°53'N; 1°03'E	0.61	19.7	14.2	13.3	13.1	14.4	16.3	20.5	23.8	24.9	23.8	19.8	18.1	
BC12	40°03'N; 1°51'E	0.62	19.9	14.2	13.3	13.1	14.4	16.3	20.5	23.8	24.9	23.8	19.8	18.1	
BC10	40°58'N; 2°09'E	0.65	20.8	14.2	13.3	13.2	14.5	16.7	20.1	22.9	24.3	23.5	20.6	17.7	
BC8	40°23'N; 1°23'E	0.61	19.8	14.2	13.3	13.1	14.4	16.3	20.5	23.8	24.9	23.8	19.8	18.1	
BC5	42°19'N; 3°41'E	0.63	20.3	13.6	12.1	12.0	13.7	14.8	18.1	20.8	22.2	21.0	20.6	15.8	
BC15	41°57'N; 5°56'E	0.59	19.3	13.9	13.3	13.2	14.3	16.5	19.7	21.7	22.8	22.1	20.6	17.3	
Mean		0.59	19.6	14.0	13.3	13.1	14.4	16.2	20.0	22.9	23.9	22.8	20.1	17.6	

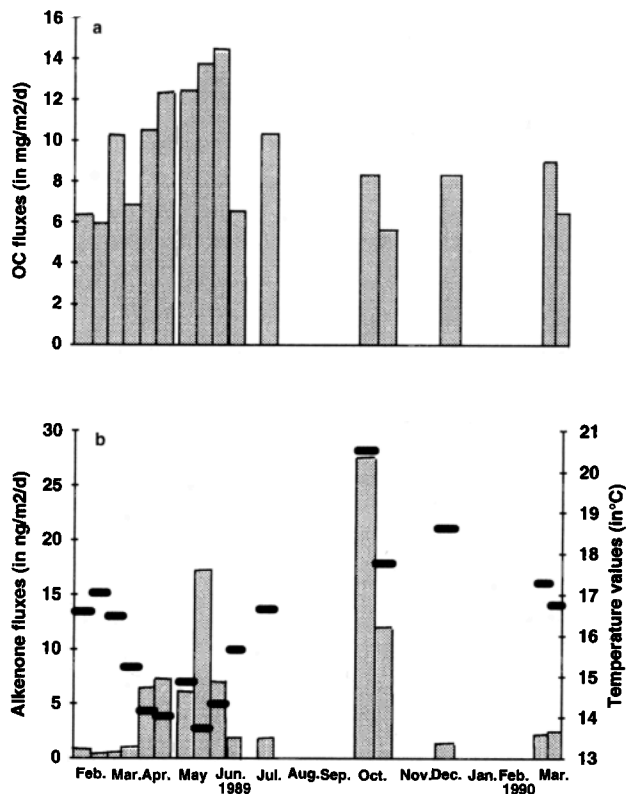


Figure 2. Temporal variations of (a) the organic carbon flux, (b) alkenone fluxes. Estimated temperatures calculated from the calibration equation: $U_{37}^K = 0.041T - 0.21$, $r^2 = 0.97$, $n = 20$ [Ternois *et al.*, in press] are also reported (thick dashes).

February and decreased during April, May and June, to about 14°C. These values were lower than expected from surface water temperature in the spring months (figure 3). This indicates a deepening of the depth distribution of alkenone-producing phytoplankton [Ternois *et al.*, in press], consistent with the similar production patterns observed by Prahl *et al.* [1993] in the NE Pacific. Alkenone-producers live in the upper euphotic zone when nutrients are not limited. As primary production continues in spring, surface waters become depleted in nutrients and alkenone producers then grow in subsurface waters where sufficient nutrients are available. In summer, alkenone fluxes decline due to the nutrient depletion in the euphotic zone, as the thermocline builds up. In October the nutrient supply restored by regeneration, and possibly also the deepening of the mixing layer replenish surface waters. Alkenone production rises again and reaches its highest value. Temperature estimates derived from U_{37}^K are those measured in surface waters at this time of the year, around 18–19°C (figure 3), indicating that alkenone production predominantly occurred in surface waters again. This inference is supported by the vertical profiles of alkenones in the water column [Ternois *et al.*, in press].

Our results suggest that the production pattern of alkenone producers may differ from that of the overall primary production in the Mediterranean Sea. However this feature needs to be confirmed by longer-term trap series to ensure that high fall fluxes are recurrent events of the coccolithophore production cycle.

Core Top Data

The occurrence of alkenones in sediments demonstrates that they can partly survive degradation. Although alkenones may experience some degradation, evidence indicates that the U_{37}^K values remain unaltered [Prahl *et al.*, 1989; Madureira *et al.*, 1995]. Temperature estimates were calculated from the U_{37}^K values measured in each core-top using the Mediterranean calibration established by Ternois *et al.* [in press]. Temperature estimation accuracy is $\pm 0.44^\circ\text{C}$. Temperature values ranged from 18.1°C to 20.8°C ($\Delta T = 2.7^\circ\text{C}$, $T_{\text{mean}} = 19.6^\circ\text{C}$) (Table 1). They were compared to monthly sea surface water temperatures [Levitus, 1982] at each core-top location to determine, site by site, which season is most closely recorded by the sediment signal (Table 1). Except for two samples (BC4 and BC11) for which data were not available, temperature estimates are similar to those encountered in surface waters in October and/or June. As discussed above, time-series of sediment trap data have shown that in spring alkenones were produced deeper in the water column, recording temperatures comprised between 14 and 15°C. If so, the alkenone exported from the euphotic zone at that time can not account for the observed temperature estimates derived from sedimentary U_{37}^K . In contrast, temperatures reconstructed from the sediment traps in October are closer to sedimentary U_{37}^K index, for each site (except for BC15). This result agrees with the large autumn production observed in the trap series. At this time of the year, the alkenone flux is higher and therefore may represent a major input to the marine sediment which would more significantly imprint the U_{37}^K values preserved in the sediments, than low flux periods. However, we cannot rule out the possibility that sedimentary U_{37}^K may also reflect annually-integrated SST. Mean annual SST, calculated at station 1 based on U_{37}^K measurements in each cup of the trap weighted for alkenone fluxes, was estimated to 17.3°C. This value was by 1°C lower than the estimated "production" temperature derived from the U_{37}^K measured in surficial sediment at this site ($T = 18.3^\circ\text{C}$). This may be primarily explained by the fact that the sediment trap record is incomplete and, noticeably, that the summer months, characterized by higher SST, are missing in the sediment trap record. This would lead to underestimate the annually

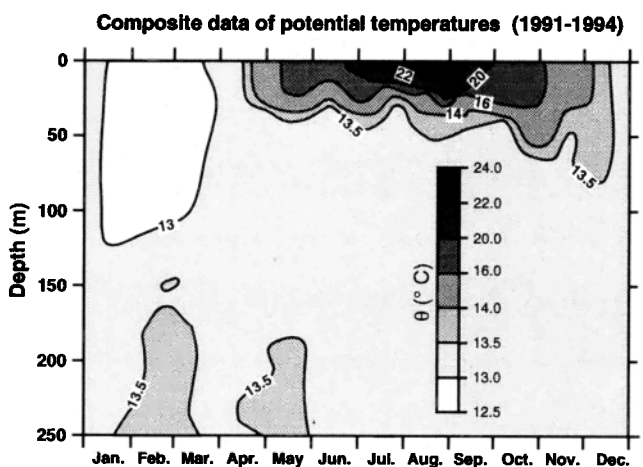


Figure 3. Composite of monthly potential temperatures (in °C) from 1991 to 1994 in the first 250 m depth, at the sediment trap site, station 1.

integrated temperature signal. Similar results were obtained when comparing SST derived from the core-top U_{37}^K with those calculated from Levitus Atlas monthly temperatures weighted by alkenone fluxes from the sediment traps. SST derived from core-top U_{37}^K values were also 1°C higher. Although other reasons may be invoked [Prahl *et al.*, 1993], such as the possibility of a more efficient remineralization during high production periods, in the water column and/or sediment, the limitation of the sediment trap sampling do not allow further discussion on the observed temperature offset.

Conclusions

The comparison of alkenone temperature estimates derived from surface sediment with sediment trap data and water column temperature profiles in the euphotic zone indicated that the sedimentary alkenone temperature signal does not reflect spring bloom SST but rather annual integrated SST with a strong imprint of fall temperatures, when coccolithophore production is more important. Annually integrated temperatures calculated from the sediment trap data were 1°C lower than those recorded in surficial sediments at station 1 and other sites of the Northwestern Mediterranean basin, possibly due to the summer months missing in the trap record. Our data suggest that inferences based on core-top U_{37}^K values must consider the seasonality and depth of the alkenone production. This study points out the applicability of alkenones in paleoclimatology and paleoceanography, and emphasizes the needs to better constrain this tool by further investigations on interannual variability of the coccolithophore production.

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